Environment Canada

A SUMMARY REPORT OF "CO-OPERATIVE PROGRAMME OF RESEARCH ON THE BEHAVIOUR OF HAZARDOUS WASTES IN LANDFILL SITES"

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"CO-OPERATIVE PROGRAMME OF RESEARCH ON THE BEHAVIOUR OF HAZARDOUS WASTES IN LANDFILL SITES"

A SUMMARY REPORT

1.0 INTRODUCTION

In the spring of 1979, a federal-provincial committee of representatives from several environmental departments in the Atlantic Region was established to provide advice on the selection of a hazardous and toxic waste disposal site in the region. Specifically, the Committee was directed to pre-screen a number of proposed federal and provincial crown land sites from the point of view of their suitability for development of a hazardous and toxic waste disposal facility. Once this pre-screening task had been accomplished, the Committee's next task was to select a series of sites for more detailed examination. At this stage, such variables as the hydrogeological properties of the site, potential deleterious impacts on downstream resources; and the possibility of site engineering work to minimize these impacts were considered.

During the course of the Committee's deliberations, reference was often made to the report "Co-operative Programme of Research on the Behaviour of Hazardous Wastes in Landfill Sites" (Final Report of the Policy Review Committee, Department of Environment, London, U. K., 1978). Because of the comprehensive nature of this report and its perceived relevance to the Committee's mandate, it was decided that a summary of the report should be prepared in an attempt to glean insights from the U. K. experience which might be of use to the Committee in the completion of its work.

In particular, the summary of the U. K. study was directed to focus on the following aspects of relevance to the Committee's mandate:

1. The site selection or pre-screening methodologies and techniques which were used.
2. Actual on-site investigations undertaken by the U. K. researchers.
3. The results of laboratory or simulation tests conducted at the various sites studied.
4. The manner in which the foregoing information was evaluated to determine the need for any on-site engineering needed to minimize environmental impacts at each site.
5. The operational successes and failures encountered at each site with respect to minimizing these impacts.
6. Any guidelines generated within the U. K. research which might be of value in the Canadian context.

The following report presents the results of this summary. As it turned out, it was not possible to address all of the above points directly, since the U. K. report itself dealt with some of them only circuitously. However, an attempt was made to interpret the U. K. results in terms of all the factors listed above, even if only a general interpretation was possible.

The summary is organized in much the same way as the U. K. report itself. That is, it first outlines the on-site investigations, field experiments and laboratory investigations that were undertaken. This is followed by a review of all results and findings of all studies

undertaken . The results are then discussed in terms of the physical and chemical processes that were observed to be occurring in the landfill sites. The next sections describe the processes on-going in the landfill itself; in both the unsaturated and saturated zones beneath the landfill; and in the geologic sub-strata. The final two chapters present the summary and conclusions of the exercise.

2.0 PRELIMINARY INVESTIGATIONS

An office assessment, which preceded the field work, involved the collection and appraisal of all available information relating to the hydrogeology and waste disposal history of each landfill site. The initial study, which consisted of the use of geological and topographical maps plus the use of records of existing wells and boreholes, provided information on the sub-surface geology, thicknesses of unsaturated zones and the regional ground water flow patterns. Information pertaining to the nature and timing of deposited wastes was obtained from site operators, local authorities and aerial photographic records. Exploratory site investigations followed to determine the validity of the available information and for planning detailed investigations, by implementing test drilling and sampling programs.

3.0 ACTUAL SITE INVESTIGATIONS

3.1 Exploratory Program

Shallow boreholes were drilled within the landfill sites in grid patterns during the exploratory phase of the program in order to determine the outline of each landfill and to obtain soil and rock samples which were later subjected to laboratory analysis to locate and identify hazardous substances. In addition, at least three boreholes were drilled downgrade from the landfills to determine local groundwater flow patterns, and to define the presence of any perched water tables. This was of considerable importance since perched water flow conditions can vary significantly from the regional groundwater flow pattern, depending upon the former inclination of the impermeable clay layers located within the sand deposits (permeable layer). That was the extent of the exploratory phase. No chemical analyses were done on water in the boreholes, nor were there any analyses carried out on materials in the boreholes lying below the water table.

The holes were drilled by rapid drilling techniques, using continuous flight auguring and/or percussion drills. Holes drilled through the landfill were taken down to the base of the fill and then permanent casing was inserted and grouted in. A two meter thick cement plug was placed at the base of the boreholes to prevent the movement of leachate from the landfill

to the unsaturated zone below. The holes were then deepened by drilling through the grout plug and into the unsaturated zone for the purpose of collecting samples. The boreholes were sealed with impermeable material after the sampling and exploratory work were completed.

3.2 Detailed Site Work Program

The main portion of site exploration was much more extensive than the exploratory program. It involved deeper boreholes, more detailed sampling and better placement of borehole locations, based on the preliminary exploratory work.

Boreholes were drilled within 5 to 10 meters of the water table in landfill sites located on top of unconfined acquifers and unsaturated zones (although it would have been preferable to have drilled at least to the water table to get a complete pollution profile). Penetrations were extended below the water table in other circumstances to acquire a depth profile of any pollution underneath the sites. Precautions were taken to avoid or minimize pollution of bedrock acquifers.

A pattern of boreholes was also drilled on the perimeter of the sites, at various distances and to depths which were necessary to define the extent of any pollution plume. No information is presented in the study concerning any specific procedures followed to locate the boreholes. It should be stressed that emphasis was placed on the collection and analysis of water samples, and the systematic collection of solid samples

at known depths and from adjacent strata. These samples were later subjected to chemical and physical analysis. Gas samples were also collected from bore-holes and later analysed as drilling progressed. Visual examinations and laboratory physical analyses were carried out on rock cores, as was geophysical logging of the boreholes. Rock cores were examined for lithology differentiation, zones of potentially high permeability (fractures and fissures) within the rock, or for coarse-grained horizons in fine-grained rock. Porosity, centrifuged specific yield, and intrinsic permeability in the horizontal and vertical directions were evaluated on selected cores using standard methods. Permeability tests were also done on unconsolidated samples. Theoretical travel times through unsaturated zones were determined in the laboratory by analyzing the hydraulic properties of aquifers and by using a modified equation of Darcy's Law. The values calculated were later compared with values observed in the field.

The geophysical logging of boreholes was necessary in order to provide pertinent information on the groundwater flow system and for the identification of any potential pollutants at various levels in boreholes. According to the report, "changes in lithology and the presence of permeable horizons and fractures zones can be identified from lithological logs (gamma, caliper and formation resistivity logs)"[1]. "Preferential movement within borehole standing water can be indicated using

1. J. Sumner and others, Hazardous Wastes in Landfill Sites (London, 1978), P. 49

fluid logs, such as temperature and differential temperature logs, fluid conductivity and heat-pulse flow meter logs."[2] "The combined use of standard lithological and fluid logs allowed the determination of major hydrogeological influences of the movement of contaminants in the vicinity of a landfill."[3]

4.0 FIELD EXPERIMENTS

Studies were carried out in the field on the movement of leachate through unsaturated zones. This was accomplished by constructing bottomless rectangular concrete boxes called lysimeters, which were filled with a material known as Lower Greensand, which consists of slightly clayey fine sands found in Oxfordshire. A roof was placed over the boxes to keep out precipitation. Synthetic leachates (1) a heavy metal, (2) an organic, and (3) an anionic type were each sprayed over the top of the fill material and the attenuation of leachate components was noted by inserting suitable probes at various levels. The object of the experiment was to determine the attenuation of leachate components in passing through unsaturated zones to the water table by simulation.

Access tubes for neutron moisture probes were also installed in these lysimeters in order to make indirect measurements of moisture content changes (none of these were

2. Ibid

3. Ibid, P. 50

ever installed at any of the landfill sites themselves).

The so-called monolith lysimeters consisted of undisturbed monolith cores of chalk, sand and gravel 0.65 m^3 (0.65 meters cubed), extracted from the ground and then instrumented. Domestic (household) waste was placed over the top of the monoliths to create aneorobic conditions within the core. The monoliths were then irrigated with synthetic leachates, and the attenuation of leachate components was studied. A prime objective was to compare results obtained with those of the large scale lysimeters.

Groundwater monitoring was also carried out to relate changes in the rate of infiltration caused by rainfall and/or disposal of liquid wastes, in addition to changes in biological, chemical and physical conditions of the waste with respect to time.

5.0 LABORATORY INVESTIGATIONS

Bench scale studies on typical wastes discarded at the various landfill sites were carried out. Solvent evaporation and adsorption on to the wastes at the landfill; the processes involved in dissolving metals in primary cell wastes; the removal of arsenic from clays, limes and iron sludges; as well as the treatment of arsenic effluents, were investigated. Furthermore, the adsorptive capabilities of wastes with respect to inorganic cations and anions were examined.

Pilot-scale experiments were also conducted on an aqueous cutting oil-emulsion, a cyanide heat-treatment waste and a

metal hydroxide waste. The primary objective here was to determine the concentration and amount of industrial waste in each experiment, and to ascertain what happened to that part which was not leached out. The large scale experiments were carried out in rectangular boxes, each $5m^2$, and the smaller ones were done in PVC (polyvinyl chloride) pipes, $0.07m^2$. They were all opened at the top so that the water received and leaches produced were recorded. Air was blown in at the bases to permit the experiments to be performed under aerobic conditions. Studies were also done under anaerobic conditions without air. For each waste studied, two tanks and two pipes were used. The top layer of waste in both containers held pulverized household waste ranging from 0.61 meters to 0.7 meters, which was followed by a layer of industrial waste 0.04 meters thick. The bottom layer was also pulverized domestic waste, 0.84 to 0.94 meters thick. The leachates produced in these experiments passed through quartzite chippings 0.16 meters thick located at the bottom of the containers, before they were collected in bottles for analysis.

Experiments were also carried out in the laboratory in saturated small columns containing sand and clay from the Lower Greensand formation to study the adsorption of heavy metals; the behaviour of mercury, chromium and cutting oil in sand and clay; and the behaviour of phenol, lithium and chloride to provide data for the calibration of mathematical models of leachate movements. Larger columns were used to investigate the adsorption and desorption of metals as well as the degradation of phenol. The object was to compare results with similar experiments carried out in the field using larger scale models.

6.0 LABORATORY ANALYSIS

6.1 Field Experiments

The synthetic "cationic" leachate contained mostly heavy metals and organic acids. Consequently, the principal laboratory analyses involved heavy metals and TOC determinations. Other elements, including lithium, (used as a tracer) were determined as well.

The synthetic "organic" leachate consisted of phenol, dichlorophenol, aniline and acetate. These chemicals are often disposed of in landfill sites.

Sulphate, choride, nitrate and phosphate were contained in the aqueous, inorganic, "anionic" leachate. The corresponding cations were sodium, potassium, ammonium and rubidium (another tracer).

6.2 Exploratory Borehole Samples

The procurement of bulk samples and subsequent chemical analyses were done solely to produce a qualitative identification of hazardous substances from boreholes drilled in the landfill, rather than for quantitative determinations.

6.3 Main Program of Site Work

In contrast to the exploratory site investigations, the main program involved more detailed sampling and testing. For example, a wide range of chemical analyses was carried out to ascertain, as far as possible, the full extent of any aquifer contamination as a result of the disposal of waste at any

particular landfill site. Both liquid and solid samples were collected from boreholes within the landfills around the landfills, and away from the landfills. These samples were analyzed for TOC (total organic carbon), specific substances which were known to be in the waste, and for the usual components of waste. A primary objective was to determine the overall distribution of contaminants during the time of drilling. In addition, undisturbed samples of rock or fill were gathered from pre-determined depths and centrifuged. The interstitial water released therefrom was then analysed for contaminants. It was found that clearer sample results were obtained from porous rock cores at different borehole depths than from unconsolidated coarse sands and gravel.

Samples procured from the main site investigation program were analyzed as soon as possible. When storage was necessary, solid samples were kept at -18°C, and subjected later to analysis for total metals, oil, phenol, individual metals, PCBs and other hazardous substances. Some liquid samples were kept at either 4°C or room temperature, and analyzed within 48 hours of sampling for TOC, ammonia and oxidized nitrogen, phenols and metals. Other liquid samples, from which air was excluded, were stored at 4°C and analyzed later for oil, phenol, PCBs and for additional hazar- dous organic compounds (dissolved oxygen, electrical conductivity and pH determinations were done in the field).

Oil contamination of solid cores and interstitial water did occur during the drilling program. As a consequence, the outer 20 - 30 mm core was removed from the 110 mm cores before the analyses were begun.

7.0 RESULTS AND FINDINGS

7.1 General

The main concern in the disposal of hazardous wastes in landfill sites is to minimize environmental risks and to prevent pollution of the water resources. To achieve this objective, methods, quantities and rates used in the disposal of wastes had to be studied.

Although hazardous wastes and their ramifications took prominence in the study, there were other types of wastes which had to be taken into consideration as well, because of the potential for reactions between components of hazardous wastes and other waste substances.

These other types of waste included liquids, sludges and solids, and mixtures of complex organic and inorganic substances which derived from a variety of sources.

Methods of disposing of hazardous wastes were studied with respect to short-term handling problems, escape of pollutants from the site, and whether or not the wastes remained at the sites unchanged.

Disposal practices varied greatly. For example, industrial wastes were either disposed of alone, or mixed with other wastes; liquids were either disposed of in lagoons or in trenches excavated in solid wastes. Pure liquid wastes were disposed of at four landfill sites, whereas liquid plus solid wastes were deposited in four others. One site contained chromium sludge mixed with liquids, while another contained a paint sludge and a phosphate sludge. Tars, asphalts and other sludges (printing ink and

hydroxides) were all placed together at other sites. Some hazardous wastes were disposed of in either cylinders and drums, or in capsules. Lagoons were either partially or completely in-filled.

Problems arose at some sites when compaction of the landfills caused liquids to ooze out, overspills formed lagoons, and ponding occurred during heavy rainfalls when the nearby land was saturated. At one site, a major lagoon overflowed to a nearby field despite periodic cleaning out of the settled silt sediment.

Some sites had facilities installed for oil recovery while at other sites, the oil formed immiscible layers on the lagoon surfaces. Neutralization was evident at some sites, and at one site liquid wastes were neutralized before disposal at sea.

Rock fill, boulders, rubble, clay topsoil, and even sewage sludge covered some sites, while seeded topsoil covered others. At one site, the lagoon liquid was treated with a chemical fixation process which formed a gel hard enough to support vehicles.

The organization of the material in this report is based on the physical, chemical and biological processes acting on the leachate, as it travels through the landfill site, from the top of the landfill to its saturated zone or water table. In this way, the significance of the landfill interior zone, the unsaturated zone and the saturated zone, in attenuating the contaminants in the leachate, is emphasized.

7.2 Landfill Interior

7.2.1 Physical Parameters

The temperature of the interior was higher than the ambient temperature due to the breakdown of organics and other substances by micro-organisms. Initial higher temperatures resulted from aerobic degradation of waste, while subsequent lower temperatures were due to anaerobic reactions.

The amount of moisture in waste will depend on the degree of water saturation within the landfill as well as on its physical properties. Moisture content of the wastes at the sites investigated varied considerably, and ranged from 5 to 69 percent.

Densities of uncompacted, undried household waste in pilot-scale simulated experiments varied from 420 to 640 kg/m^3. No figures were available with respect to the actual landfill sites.

7.2.2 Microbiological Activity

Micro-organisms which operate within the landfill and promote biochemical reactions caused elevated temperature as compared to ambient air or underlying strata temperatures, and the formation and evolution of methane and carbon dioxide gases as well. Leachate composition was also affected by higher temperatures because of increased evaporation and decreases in viscosity.

One landfill site was investigated with regard to the identification of micro-organisms. Those found in most abundance were coliforms, followed by fecal streptococci, and two types of pasturella spp, two types of chromo-bacterium spp, pseudomonas

aeruginosa, proteus vulgaris, bacillus subtilis. Yeasts and fungi were present in very small numbers. Micro-organisms were found in unsaturated material where the pH ranged from 4.8 to 9, and were absent from saturated material where the pH was 2. Their numbers decreased with increasing depths of the landfill, due to the lower pH values and decreasing amounts of organic wastes.

Leachate produced from pilot-scale simulated landfills and from partially aerobic units was observed to be yellow-brown, odorless and turbid at first, but it became clear after a year. Anaerobic units produced leachates which were yellow-brown and turbid and had a strong odor.

At the working faces of landfills, where there is a plentiful supply of oxygen, aerobic oxidation of the organic waste occurred, and the ultimate products formed were carbon dioxide, water, sulphates, nitrates and phosphates. Intermediate products, such as acetates, were also found on occassion. However, the anaerobic microbe population increased, progressing from the face of landfills toward the interior, due to the depletion of oxygen. Sulphates, nitrates and carbohydrates become oxidants in the reduction--oxidation reactions. The ultimate products of anaerobic biodegradation are methane, carbon dioxide, hydrogen sulphide and water. Sulphates are reduced to foul smelling hydrogen sulphide. Intermediates formed are acetic, propronic and butyric acids, acetone, acetaldehyde and ethyl alcohol. Anaerobic gas production was confirmed in several boreholes within the landfill sites.

Metal sulphides and intermediate products were confirmed as components of the leachates from actual landfill sites and experimental units.

7.3 Chemical Processes

The chemical processes active within landfills are: (1) neutralization, (2) precipitation and complexation, (3) oxidation and reduction, (4) Volatilization, (5) Solubility and (6) sorption.

7.3.1 Neutralization

It is necessary to neutralize acid and alkali waste before discharging them into water courses. Excessive acid or alkali waste is harmful to fish and other aquatic life. At one site, aqueous acid and a solid alkali were mixed together in silt trenches to achieve at leash partial neutralization. At other sites, lime was added to acid waste to obtain neutralization. Tests showed that domestic (household) waste had the capacity to neutralize acids.

7.3.2 Precipitation and Complexation

The solubility of heavy metals is primarily controlled by precipitation, although further reduction is accomplished by absorption or ion exchange. Heavy metals were often deposited in the landfill sites as sparingly soluble oxides, hydroxides and phosphates. The presence of any heavy metal in the leachate is controlled by the solubility product of the "insoluble" compound of which the metal is a part, besides what is removed from the leachate by absorption or ion exchange. Additional solubility of the metal in the leachate is accomplished by complexation, for example, by the presence in the leachate of hydroxyl and cyanide ions. That is, the solubility of the metal is increased because the solubility of the metal ion plus the metal complex ion is more

than the solubility of the metal ion alone in solution, as defined by the solubility product.

Hydroxides, phosphates and cyanides form complex ions with metals in solution. Many landfill sites were deficient in oxygen, and contained anaerobic decomposed matter and sulphides. Many metals form slightly soluble sulphides as was proved through investigations at the landfill sites and simulated landfill site experiments. At sites containing metal hydroxide sludges, no appreciable quantities of metals were found in the leachate. Pilot scale landfills demonstrated that cyanide increased the solubility of heavy metals by complex formation. The concentrations of heavy metals in leachates from cyanide contaminated landfills were higher than those without cyanide.

7.3.3 Oxidation - Reduction

An example of chemical oxidation and reduction operating within a landfill site is provided at one site where sodium chromate and thiosulphate were deposited in the same lagoon. The pH was 10 and no reaction occurred. If however, the pH were reduced to near neutral, the reduction of chromium VI to chromium III with the precipitation of chromium hydroxide would be expected to take place. In laboratory experiments, chromate concentrations decreased in the presence of household waste from 100 mg/l to 25.5 mg/l in one week, and to 10 mg/l after 15weeks with a pH range of 6 to 6.5, which is in accord with the reduction of hexavalent chromium to trivalent chromium because of the decrease in pH to the acid side of the scale.

7.3.4. Volatilization

Low boiling point dry cleaning solvents were shown to evaporate from household waste, and these solvents were abandoned from use in synthetic leachates in lysimeter experiments because of this phenomenon. However, if sufficient quantities are deposited at landfill sites, some will migrate downwards through the fill.

Mercury vapor was detected over landfill sites containing mercury waste. According to laboratory tests carried out at 100°C, only 0.2% of the mercury in household waste was volatile.

Carbon dioxide in landfills assists in maintaining the pH below 9. At pH below 9, the production of hydrogen cyanide takes dominance over the cyanide ion. Hydrogen cyanide gas was detected in boreholes at two landfill sites and also in simulated pilot scale operations. Moisture or water absorbed some hydrogen cyanide which prevented its release into the atmosphere, whereas the higher than ambient temperature in the waste tended to increase its release to the atmosphere.

7.3.5 Solubility - Organic Substances

Mineral oils, halogenated organic compounds, including PCBs, and other chorinated hydrocarbons, which are slightly soluble in water, were investigated during the program. At the landfill sites examined, the highest concentrations of these components were found in the oil phase. Oil and halogenated hydrocarbons are mutually miscible. PCB Aroclor 1254 has been reported to be soluble in water to the extent of 0.1 to 10 mg/l. Tests on leachates from one landfill site gave a value of 0.5 mg/l.

7.3.6 Sorption

Phenols were strongly absorbed by household waste, by adsorption and furthermore, the process was reversible. That is, phenols were easily set free by leaching with weak carboxylic acid solutions. In actual landfill sites, phenols could only be adsorbed a short time by the waste, before being released by the introduction of a weakly acidic solution to the landfill.

Investigations carried out at some landfill sites showed oil is absorbed by waste, but this phenomenon decreased with depth. The highest concentration reported was 7% oil.

Clays can readily remove metal ions from solution by adsorption. It was shown by experiment that calcium montmorillonite (fullers earth) was more effective in removing mercury from mercuric chloride solution than illite. Boulder clay was the least effective of these substances.

7.3.7 Leachate Production and Composition

The volume of leachate provided within the landfill can only be determined with any degree of accuracy under carefully controlled experimental conditions. However, estimates were made using the water-balance equation as applied in the field of hydrology for determining recharge rates to groundwater.

The composition of leachate will depend on many factors. These factors include the amount of a particular substance in the waste; its physical and chemical properties; other wastes placed within the landfill; and hydrological factors. Large variations in TOC, ammoniacal nitrogen, metals, pH and other constituents were found in the landfill sites examined.

In anaerobic pilot-scale simulated landfills, which contained household waste mixed with metal hydroxides, oily and cyanide wastes, produced leachates which were typical of waste collected from households. For example, TOC was about 8,000 mg/l, of which four-fifths were short chain carboxylic acids; there were high BODs and CODs; nitrogen concentrations ranged from 300 - 600 mg/l; ammoniacal nitrogen ranged from 200 - 400 mg/l; and nitrates (oxidized nitrogen) were up to a miximum of 6 mg/l. Iron, manganese and zinc ranged from 66 - 250 mg/l, 3.5 - 9.2 mg/l and 0.4 - 32 mg/l respectively. The pH's ranged from 7.1 to 9.5

7.3.8 Ground and Landfill Interfacial Reactions

The significant attenuating mechanisms which occur at the interface are filtration of particulates, adsorption on gel precipitates and precipitation reactions. One landfill site which was investigated showed significant reductions in leachate components at the interface by the adsorption mechanism because of the presence of clay. At other sites, rapid biodegradation of TOC produced short chain carboxylic acids in gravel, but there were no significant effects on the removal of persistent organic compounds such as phenol and metal ions. At chalk surfaces, carboxylic acids reacted with calcium carbonate, liberated carbon dioxide, increased the pH and formed calcium salts of the organic acids.

Organic compounds appeared to inhibit the diffusion of non-absorbed species by the blinding of pores which resulted from the precipitation of organic compounds. However, after the organics were biodegraded, rapid diffusion of chloride occurred. The blinding pores phenomenon was also demonstrated in the simulated

experiments. Leachate was forced to form on top of the lysimeter and was surrounded by a whitish biomass. In some landfills, pore-blinding caused leachate to move out and form ponds.

8.0 UNSATURATED ZONE, LEACHATE TRANSPORT AND ATTENUATION

8.1 General

Ten of the twenty sites examined had unsaturated zones. The thicknesses varied seasonally, and even daily, in response to withdrawals and recharging of groundwater, but the average variation was approximately 4 meters to 40 meters, and the most prevalent thickness was in the 20 - 30 meter range.

8.2 Transport

Groundwater flow through the unsaturated zone is essentially vertical, except in perched water zones where it is forced to move laterally. In the unsaturated zone, flow can only occur when there is a water phase. Two separate types of flows can occur in the unsaturated zones; namely fissure and intergranular flows. Fissure flow was identified in the lower parts of chalk at one landfill site. The rates of flow for three different types of unsaturated formation were as follows: clay and sand 0.8 meters/-annum, bunter pebble bed 2 meters/annum and chalk 255 meters/-annum. The high value for chalk was due to fissure transmission, wheras in the other formations, water transmission was by intergranular movement. Thirteen of the twenty sites examined belonged to the medium rate of transport category.

8.3 Attenuation

The attenuation process may also be categorized depending on the chemical activity of the formations. For example, in clay the attenuation processes were adsorption and filtration. In one of the lysimeter experiments a heavy metal, consisting of 100 ppm of each of the following: zinc, cadmium, chromium, nickel, copper and lead, was applied at a rate of 2 millileters per day to the top of the lysimeter. After 420 days of irrigation, none of the heavy metals had reached a distance 400 mm below the surface. In chalk, there were biodegradation and chemical buffering. Comparison of results between a monolith lysimeter and a landfill site, both containing lower chalk, gave similar results. Carbon-containing compounds such as carboxylic acids and phenols were biodegraded; magnesium, potassium and sodium were exchanged for calcium. Formations such as quartzite which had fissures, and sand which was lithologically uniform, provided little or no attenuation in the unsaturated zone.

8.4 Dilution

Dilution is the result of dispersion and diffusion, and both are thought to be active in the unsaturated zone. However, there is difficulty in measuring and distinguishing it from other alternating mechanisms or processes. Chlorides are attenuated by dilution rather than by any other process. In a lysimeter experiment, the chloride concentration remained constant, equal to the applied concentration in the leachate, over the whole study section. Sodium and sulphate ions acted in a similar manner, but were

slightly delayed because of the ion exchange mechanism. In two actual landfill sites studied, the chloride ion concentration remained unchanged in the whole of the unsaturated zones, but approched background levels in the saturated zones.

8.5 Gas Exchange

Oxygen is consumed in the unsaturated zone underneath the landfill because of chemical oxidation and microbial respiration. Oxygen replenishment is very slow in the intergranular flow regime, but occurs freely in fissured strata. The replenishment takes place by isothermal molecular diffusion, lateral influx from any perched water zone, and by diffusion through capillaries leading from the main water table.

In an experiment conducted in one lysimeter with a constantly applied leachate rate, aerobic degradation initially occurred, and the gas volume analysis indicated 16 percent carbon dioxide and 2 percent oxygen. However, anaerobic decomposition of leachate set in with the production of methane gas due to the depletion of oxygen. The methane gas concentration increased to 12 percent at the same time, around the 400 day mark of testing. At several of the landfill sites investigated, dissolved oxygen levels in groundwater, which shows indirectly the degree of gas exchange occurring in their vicinities, were much less than background levels found outside their perimeters.

8.6 Temperatures

Temperatures in the unsaturated zones were 10 - 20^{o} higher than groundwater temperatures because of microbial activities.

The effect of the temperature rise is to increase the evaporation rate of the leachate, thus increasing its concentration and also decrease its viscosity which assists in the initial migration of oily substances from the site.

8.7 Immmiscibility and Filtration

Oily substances mixed with solid wastes have the capability of forming an emulsion with the infiltrating water which enters the unsaturated zones. During the investigations, traces of immiscible liquids were found in the saturated zones because of the hydraulic continuity existing between the landfill water table and the saturated zones by way of recharge mounds. It is believed that in cases of significant thicknesses of unsaturated zones, there exists a capability of dispersing immiscible liquids by the sorption process, and by retention in the intergranular media.

8.8 Biochemical Factors

The results of lysimeter and monolith experiments and also actual investigations of the unsaturated zones indicated that both aerobic and anaerobic degradation of leachate components occurred. Whether one or the other process took place depended on such factors as permeability of the materials in the unsaturated zones and how close it was to the water table. Even small scale variations in the infiltration pattern can change faculative-anearobic respiration to predominantly aerobic, and vice versa.

Elements such as carbon, nitrogen, oxygen, hydrogen, phosphorus, sulphur, potassium and other trace metals become a part of the biomass of microflora and hence promote the growth of slimes which put a limit on pore volume and delay the attenuation mechanisms.

8.9 Chemical and Geochemical Factors

The main types of chemical reactions likely to occur when leachates pass through the unsaturated zones are: Complexation, acid-base, oxidation and reduction, precipitation and co-precipitation, and ion exchange.

No positive evidence from any of the sites investigated or pilot-scale and laboratory experiments, suggested than any complexation occurred in the unsaturated zone, except at one site where cyanide was changed into the slightly soluble cyanoferrate species. However, there is no reason why complexation would not occur as much in the unsaturated zones as in the landfills. In one quarry, jarosite was precipitated due to the presence of oxygen which was previously in the form of a complex ion.

Acid-base reactions took place in one lysimeter irrigated with dilute carboxylic acid and heavy metals (pH = 5). Calcium ion concentrations increased more than three fold, 400 mm below the surface after 275 days of irrigation. Calcium ion concentrations also increased in landfill quarries with acidic pH's, where calcium montmorillonite and illite were present. At one site, a complex series of reactions involving acid-base reduction and oxidation and precipitation reactions, resulted in the formation of significant quantities of a metal deposit on fissured walls in the unsaturated chalk.

Co-precipitation also occurred in the unsaturated zones below landfills. These reactions were important mechanisms in removing heavy metals from the landfill leachates.

Ion exchange on clay minerals is another mechanism for the

attenuation of heavy metals. Laboratory experiments on 6 metals showed that lead and copper were the most strongly fixed, zinc and nickel were the most mobile, while cadmium and chromium were in the intermediate range. Mercury was also readily adsorbed by clay minerals. However, in any landfill above an unsaturated zone containing any adsorbent, such as fuller's earth, and where the environment is at least partially anaerobic, mercury will be removed, either by adsorption or by precipitation as a sulphide, before reaching the unsaturated zone.

8..10 The Significance of Unsaturated Zone Thickness

Landfill sites without unsaturated zones (i.e. where there is hydraulic continuity between the landfills, and saturated zones) and unsaturated zones up to 6 meters thick, experienced movement of leachates to the water table. At sites where there were 20 meters or more of unsaturated zones thicknesses, no significant pollution of the water table was detected. These observations, as well as those obtained from lysimeter and irrigation experiments, clearly demonstrated that the unsaturated zones reduced leachate components to significant degrees. Chemical attenuation of pollutants and biochemical degradation of organics were very beneficial because many contaminants were removed before reaching the saturated zones. Besides the character of the rock and the absolute thicknesses of the unsaturated zones, hydrological factors of permeability, hydraulic gradient and fluctuations in the groundwater table were of significant importance for gas exchange and re-oxygenation. At three landfill sites in particular, and probably at other sites as well, the redox potential was

considered positive at the pH recorded range of 7.3 to 8.3. Because of the high fluctuations in the groundwater table, as opposed to small fluctuations, there was a tendency for soluble compounds to be oxidized and the transition metals to be precipitated as complex hydroxides and carbonates.

9.0 SATURATED ZONES

In isotropic homogenous aquifers, groundwater flows in the direction of decreasing hydraulic gradient, and the flow lines are essentially horizontal. Even in aquifers which have anistropy with super-imposed beds of differing permeabilities and porosities, the flow lines are really sub-horizontal if the aquifers are unfractured. However, vertical flow occurs in fissures, in both isotropic and anistropic aquifers. Vertical flow also occurs at boundaries: springs, base flow discharges to water courses, in the vicinity of pumping boreholes, and in places where faulting has caused the aquifer to be lined up horizontally with impermeable layers of materials.

When the flow is laminar, the Darcy equation may be used to describe the velocity of flow of groundwater. When the leachates' physical properties differ from those of groundwater, there are essentially three different types of situations with respect to the flow of leachate:

(1) If the leachate is miscible with groundwater because of similarities in density and viscosity, then the contamination is pretty well confined to the upper few meters of the water table (except for some possible dispersion of contaminants due to the absence of vertical mixing). Five sites in the investigation

exhibited this type of behaviour.

(2) In some cases, leachates may be miscible with groundwater although their physical properties differ(for example, a chromium-rich leachate which was the case in point at one of the sites examined). Horizontal movement of the leachate would be different from groundwater because of density and viscosity variations.

(3) When oil-rich liquids form immiscible layers with groundwater, which was the situation at two of the sites examined, the migration of the oil phase through the saturated zone is inhibited and is forced on top of groundwater. When that situation occurs, the oily layer moves horizontally, obeying Darcy's Law. No attenuation by dilution is achieved because of the immiscibility of the two phases.

Attenuation of pollutants in the saturated zone is accomplished by dispersion, aerobic and anaerobic processes. Precipitation of metals occurred at certain pH ranges with oxygenated groundwater.

10.0 THE FATE OF SPECIFIC CHEMICAL WASTES

10.1 Halogenated Organic Compounds

Experiments and field investigations showed that relatively insoluble halogenated solvents can be accepted at landfill sites with household wastes if the correct quantities and rates of disposition are used. The wastes would provide suitable surfaces for evaporation and adsorption if adequate disposal practices are followed. Relatively soluble halogenated compounds , such as dichlorophenol, should not be deposited in sites which permit migration of leachates.

10.2 Cyanide

Cyanide is capable of undergoing several chemical reactions in a landfill environment, which include the conversion to volatile hydrogen cyanide; the formation of sparingly soluble complex cyanides; hydrolysis, which causes the formation of ammonium formate; the conversion to thiocyanate in the presence of sulphur compounds; and/or biodegradation, depending on the chemical environment. In the investigations carried out at the sites and with simulation experiments, it was shown that for the types of cyanide wastes studied, the processes operating within the landfill changed most of the cyanide into the above chemical substances, all of which had the result of minimizing the effects of cyanide in the environment.

10.3 Heavy Metals

The results of investigations showed that the physical, chemical and microbiological processes working within and underneath the landfills controlled or prevented the release into the environment of heavy metals contained in heavy metal wastes. Under proper disposal conditions, which involved the avoidance of co-disposal materials that would increase the water solubilities of metals, no significant contamination of the water resources occurred. Furthermore, if it is necessary to dispose heavy metal bearing waste on sensitive aquifers, consideration should be given to the use of a chemical fixation agent to contain the waste at the site.

10.4 Chromium

As discussed in section 7.3.3, at that particular site, the pH was reduced to 7.5 by dilution with groundwater and in theory, the

reduction/oxidation reaction should have taken place. The fact that it only occurred slightly showed that even at near neutral pH the reaction is sluggish.

Study of tannery waste disposed of at another site containing cationic chromium salts (for example, chromium sulphate) revealed that only low concentrations of soluble hexavalent chromium were found in the waste as compared to high anionic chromium (for example, $NaCrO_4$) found in the previous site. The oxidation of cationic chromium associated withthe tannery waste to the more soluble and toxic hexavalent anionic form failed to occur, probably due to the high pH of the liquid waste at the disposal site.

10.5 Mercury

At one site, mercury was disposited with demolition waste. This waste was close to clay containing fuller's earth, which strongly adsorbed mercury when it was in the form of mercuric sulphide or mercurous chloride. No organo-mercury compounds were found.

Other sites were investigated to determine the environmental hazards which result from the large disposition of waste containing mercury (for example, lamps and primary cells). The findings from these investigations clearly illustrated that the behaviour of mercury waste is dependent upon the process occurring within the landfill, rather than on the geology underneath the waste. Elementary mercury was found on or very near the surface of the landfill. A few meters below, mercury was either oxidized under anaerobic conditions and formed insoluble compounds, such as sulphides, or was adsorbed onto other material, especially fuller's earth. These processes prevented the migration of mercury into the leachate.

No evidence of organo-mercury compounds was found at any of the sites examined.

10.6 Phenol and Phenolic Substances

Phenolic wastes are produced in the manufacture of resins and other organic chemicals, carbonization of coal, pyrolysis of rubber, and also from the degradation of cellulosic waste in landfills.

Phenols have a great potential to contaminate water resources if released with the leachate. Phenol is water soluble, but other phenolic compounds are generally insoluble. The majority of phenolic compounds exhibit toxological effects, and therefore can kill microbial populations if present in high concentrations. In low concentrations, phenols are biodegradable.

Liquid wastes containing phenols ranging from 8 to 100 mg/l with a mean of 17 mg/l were disposed of in lagoons. When the wastes passed through lagoons in series, the concentration was reduced to 0.6 mg/l by biodegradation, evaporation and adsorption. At one site, the chemical fixation process was effective in immobilizing phenols.

11.0 THE INFLUENCE OF GEOLOGY ON LEACHATE MIGRATION

Landfill sites may be classified into three basic types with respect to geological conditions:

1. Containment of wastes and leachate.
2. Slow migration of leachate and significant attenuation
3. Rapid leachate migration with very little attenuation

11.1 Containment of Leachate

Shales, slates, mudstones, siltstones and marls which have hydraulic conductivity equal to or less that 10^{-3} meters/day belong to this category. Because of the impermeable strata provided by these materials, very little throughflow is permitted, and this phenomenon is one of the main factors which causes ponding during periods of rainfall, and also encourages intercepted drainage, without any waste liquid disposal. Ponding occurred at two landfill sites under investigation, and was associated with this phenomenon.

Fine sands and silts became impermeable in the vicinity of the landfill sites due to clogging of pores by immiscible oil and ferruginous gels, and these sands and silts behave like impermeable strata and promote ponding.

11.2 Slow Migration of Leachate and Attenuation

The geological formations which provide leachate migration and attenuation by intergranular flow are also classified as aquifers. This category can be divided into two sub-divisions with regard to fluid flow characteristics:

(1) Intergranular flow formations such as sands, sandstones, sandy clays, gravels, etc.

(2) Formations which show a significant number of fissures in addition to some capacity for intergranular storage, such as chalk, most triassic sandstones, etc.

However, both subdivisions must satisfy the criterion which is that the intergranular conductivity should be greater than the maximum rate of recharge caused by rainfall infiltration, and liquid wastes. All the attenuation processes have been already discussed.

11.3 Rapid Leachate Migration

Rapid leachate migration occurs in most fissured rocks, such as granite, carboniferrous limestone and coarse unconsolidated gravel. Flow of leachate, which is produced by rainfall and liquid waste, is rapid and localized, with very little storage or retention taking place. Dilution is by dispersion mechanism rather than by diffusion. Some chemical attentuation is possible because the leachate can cover a large area of the bedrock and oxidation is induced by turbulence. However, at one of the sites investigated the leachate passed through the fissured dolerite dyke unchanged, and a similar circumstance occurred at the Sulhamstead Irrigation Research Centre when a synthetic leachate was made to pass through plateau gravels. The reason that no reduction of leachate components occurred was due to the lack of attenuation mechanisms in the materials at these two sites.

12.0 SUMMARY

The co-operative research program undertaken to study the behaviour of hazardous wastes in landfills was carried out on twenty existing sites in England, Scotland and Wales. It should be mentioned that some of the sites were very old and are no longer in use, while others are used up to the present time. Consequently, the program did not deal specifically with the problem of selecting a landfill site for the disposal of hazardous substances. However, an office study which consisted of a review of geological and topographical maps, as well as the use of records of existing wells and boreholes, provided informa-

tion on the subsurface geology, thicknesses of unsaturated zones, and the regional groundwater flow patterns relating to the existing landfill sites. An assessment of these factors should obviously be part of the pre-selection or pre-screening process for new landfill sites.

The actual on-site investigations, which involved both the exploratory program and the detailed site program, provided most of the information about the behaviour of hazardous substances at each landfill site. The exploratory program (which consisted of a limited number of shallow boreholes) provided clues as to the location of hazardous substances, and the detailed program (which involved more and deeper boreholes) yielded information on depth profiles of any polluting substances underneath the site, and on the extent of any pollution plume. The systematic collection and analysis of solid and interstitial water samples at known depths from different strata provided pertinent information on the geologic and hydraulic factors present at the sites, as well as on the movement of pollutants within each.

Field experiments using lysimeters were conducted to determine the movement of synthetic leachates through the unsaturated zone. As the leachates passed down through the lysimeters, the attenuation of specific pollutants was monitored.

Bench scale, pilot plant studies and saturated column experiments were also conducted in the laboratory. The bench scale studies were on typical wastes discarded at the landfill sites. The adsorptive capabilities of the wastes, the dissolution of metals from various substances and the treatment methods that would be required to minimize their effects were assessed. In the pilot plant studies, attention was focussed on the concentration and quantity of industrial waste in each experiment, the amount that was leached out and what happened to the

portions that remained in the landfill. In the laboratory saturated column experiments, the adsorption and desorption of heavy metals, the behaviour of mercury, chromium, cutting oil (in sand and clay), as well as the degradation of phenols were studied, and the results attained were compared to those of the larger scale field experiments.

The information gathered in the actual on-site investigations and laboratory experiments was not evaluated for the purposes of determining the degree of engineering and/or pre-treatment that would be required for the various sites, but rather as basic data to support the research conclusions of the project. Moreover, the United Kingdom report did not deal exclusively with the issue of how best to mitigate the negative impacts of hazardous wastes on the water environments of landfill sites. The research illustrated the processes involved, rather than how these processes could or shold be modified in a management context. Although it is possible to infer the types of management actions that might offset these impacts, thc U. K. report did not deal with this issue directly, and no attempt has been made in this summary to do so either.

13.0 CONCLUSIONS

Probably the most serious environmental risk associated with any landfill operation is that the nearby water resources will become contaminated. To minimize this risk, a significant effort should be made to ensure that the site that is selected is suitable.

In general, the U. K. study found that the presence of an unsaturated zone beneath the landfill can be advantageous because it

provides a delaying mechanism during which pollutants can either be attenuated or reduced before they reach the saturated zone (groundwater).

Results of tests within the landfill interior itself indicate that micro-organisms promote biochemical reactions under both aerobic and anaerobic conditions. The chemical processes of precipitation, complexation and oxidation-reduction operating within a landfill further reduce the strength and quantity of contaminants. In addition, the physico-chemical mechanisms of sorption and ion exchange are important in reducing the quantities of certain chemical species.

Mixed mineralogies (such as clay with sand lenses and sand with clay lenses) have the capacity to retain various cations if these are present in the landfill. Also, household waste itself has a significant retentive capacity for mercury, oils and PCBs (but not for phenols) by the processes of sorption and ion exchange.

The presence of an unsaturated zone beneath a landfill reduces pollutants in the leachate to significant degrees by physical, chemical and biochemical processes, provided the correct types of rock materials are present. In clay, heavy metals are attenuated by adsorption, while in chalk, biodegradation of organics as well as chemical buffering take place. Quartzite (which is quite fractured) and sand (which is lithologically uniform) provide little or no attenuative capacity. In addition, the chemical processes of oxidation, reduction, acid-base reactions, precipitation and co-precipitation play significant roles in removing or reducing contaminants before they reach the saturated zone.

In the saturated zone, leachates and groundwater mix, although the degree of mixing will vary somewhat. Generally, aqueous wastes will attenuate more readily than oil/water mixtures. The hydrological

variables of permeability, hydraulic gradient and groundwater fluctuations are of significance for gas exchange and re-oxygenation processes. If there are large fluctuations in the groundwater table, there is a tendency for soluble compounds to be oxidized and for the precipitation of transition metals as complex hydroxides and carbonates to occur.

Site geology and hydrogeology are also key considerations in judging the degree of attenuation of leachate contaminant that is likely to occur at a landfill site. But it is important that these variables be assessed in a dynamic interactive context. That is, a given geologic formation may or may not be a positive factor in mitigating the environmental impacts of hazardous waste disposal sites. For example, a particular formation may offer the advantage of containing a form of hazardous waste which is otherwise difficult to break down or to attenuate by natural processes. On the other hand, there aredisadvantages associated with sites oriented forwards with containment. Impermeable strata can cause ponding during heavy rainfall periods or when waste liquid is disposed of. Also, fine sands and silts in the vicinity of landfill sites can become impermeable when the pores become clogged with immissible oils and ferruginous gels, and this also causes ponding. Moreover, if the containment site is placed above a confined aquifer with a high piezometric head, there can be an upward seepage of spring water into the landfill site, thereby increasing the chances of run-off and seepage to surface water resources, and also to groundwater levels outside the landfill site.

Although the U. K. study does not directly address the issue of how new sites should be selected, the following process is implied by their analysis:

1. Pre-screen sites on the basis of office studies, published data and acceptability of the sites in gross environmental terms.

2. Conduct field experiments and tests (supported by laboratory experiments under controlled conditions if possible) to determine the attenuative capacities of in situ soils, as well as their permeabilities,and other physical properties.

3. Determine whether any of the pre-selected sites is suitable, based on the previous experiments.

4. If a site is otherwise suitable but lacks the desirable geologic or hydrologic properties, then the possibility of site engineering should be considered.

Perhaps the most significant conclusion of the U. K. study is that the areal extent of pollution plumes around most of the landfills was quite restricted. Even though some of the landfills had been operating for very long periods of time, few cases of groundwater pollution from the landfills were observed in the study. This means that landfills that are designed and selected properly have a very good chance of serving their intended purpose with a minimum of environmental risk. Therefore, an overly cautious approach to the development of hazardous waste landfill sites would appear to be unwarranted. This statement is not intended to diminish the need for further research into the subject, nor should it be taken to mean that judicious consideration of both the site and the waste expected to be disposed of at the site is not necessary. Both elements are important to our ultimate understanding of the processes on-going within hazardous waste disposal sites. However, the U. K. study would appear to indicate that environmentally acceptable hazardous waste disposal sites can be developed to meet Canadian needs.